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Published in:
The Journal of Physical Chemistry Letters

DOI:
[10.1021/acs.jpcllett.7b02553](https://doi.org/10.1021/acs.jpcllett.7b02553)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2017

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Kahmann, S., Rios, J. M. S., Zink, M., Allard, S., Scherf, U., dos Santos, M. C., Brabec, C. J., & Loi, M. A. (2017). Excited-State Interaction of Semiconducting Single-Walled Carbon Nanotubes with Their Wrapping Polymers. *The Journal of Physical Chemistry Letters*, 8(22), 5666-5672.
<https://doi.org/10.1021/acs.jpcllett.7b02553>

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Excited-State Interaction of Semiconducting Single-Walled Carbon Nanotubes with Their Wrapping Polymers

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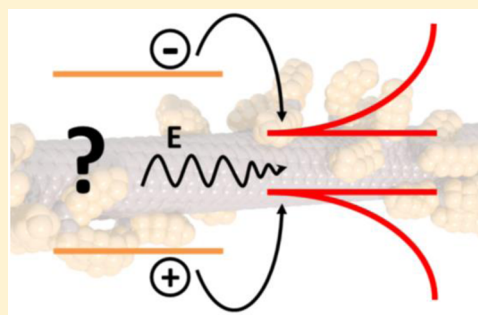
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S Supporting Information

ABSTRACT: We employ photoluminescence and pump–probe spectroscopy on films of semiconducting single-walled carbon nanotubes (CNTs) of different chirality wrapped with either a wide band gap polyfluorene derivative (PF12) or a polythiophene with narrower gap (P3DDT) to elucidate the excited states' interplay between the two materials. Excitation above the polymer band gap gives way to an ultrafast electron transfer from both polymers toward the CNTs. By monitoring the hole polaron on the polymer via its mid infrared signature, we show that also illumination below the polymer band gap leads to the formation of this fingerprint and infer that holes are also transferred toward the polymer. As this contradicts the standard way of discussing the involved energy levels, we propose that polymer-wrapped CNTs should be considered as a single hybrid system, exhibiting states shared between the two components. This proposition is validated through quantum chemical calculations that show hybridization of the first excited states, especially for the thiophene–CNT sample.



Polymer-wrapped semiconducting single-walled carbon nanotubes (CNTs) attract considerable research interest because they allow for solution deposition, possibly on flexible substrates, and are stable under environmental conditions. Crucially, the wrapping polymer not only promotes stability of the suspension but also serves as a sensitive tool to select semiconducting tubes, which are generally mixed with metallic ones after synthesis.^{1,2} This selectivity is a key reason for an improved performance of CNT electronic devices, for example, field effect transistors or photodetectors.^{3–6} While charge conduction in this composite system is commonly discussed as if the polymer chains were absent, the close proximity of the two components and their π -electron systems suggest otherwise.

Consequently, photoluminescence (PL) spectroscopy of films of polymer-wrapped CNTs often reveals a shortening of polymer PL lifetime, when compared to the neat material. This effect was previously attributed to a rapid energy or electron transfer toward the CNTs.^{7–10} It is of utmost importance to understand this interaction in greater detail, especially when developing electro-optical applications involving charge transport through networks of polymer-wrapped CNTs.

Here, we report on the photophysical behavior of polymer-wrapped semiconducting CNT films. Using a Fourier transform

infrared (FTIR) spectrometer, we measure the steady-state photoinduced absorption down to energies as low as 0.07 eV. In this spectral region, we observe the polymer's polaron absorption, which we use to monitor charge-transfer processes. Additionally, we employ ultrafast transient PL and absorption spectroscopy to further elucidate the interplay of the two components and employ quantum chemical calculations to validate our theory. As model polymers, we chose a wide band gap polyfluorene (poly(9,9-didodecylfluorene-2,7-diyl), PF12) and a polythiophene derivative (poly(3-dodecylthiophene), P3DDT) with narrower band gap, both of which are able to efficiently select semiconducting CNTs.⁵

We find long-lasting ground-state bleaches and photoinduced absorptions to form for all chiralities at all employed excitations. The strength of the respective bleaches follows the absorption spectrum, hence demonstrating that fast intertube energy transfer toward narrow band gap tubes is not dominant in our films, which is contrary to other groups' reports on similar systems.^{11,12} More importantly, we report the distinct polymer-specific polaron signature in the mid infrared

Received: September 28, 2017

Accepted: November 3, 2017

Published: November 3, 2017

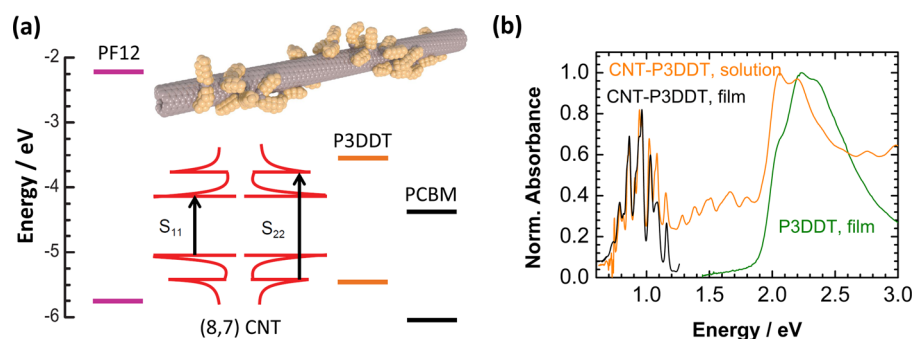


Figure 1. Energy levels of neat polymers, PCBM and a representative CNT along an illustration of a polymer-wrapped CNT (a). Absorption spectra of P3DDT-wrapped CNTs in solution and film along with a film spectrum of the neat polymer displaying their complementary regions of absorption (b).

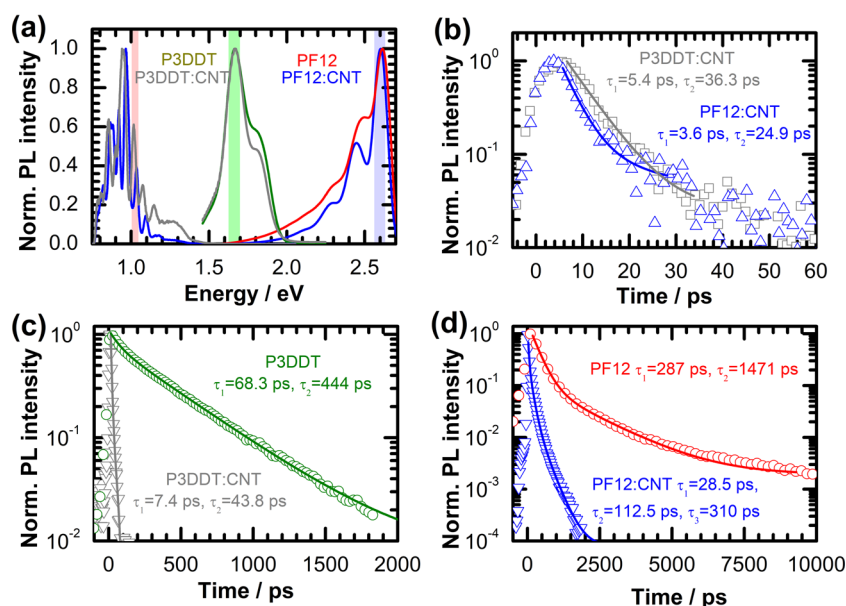


Figure 2. Steady-state (a) and time-resolved PL (b–d) spectra of polymer-wrapped CNTs upon excitation with 400 nm. Vertical bars in panel a indicate the windows from which the transients were extracted. Panel b displays the emission of the CNTs; panels c and d display the emission of polymers P3DDT and PF12, respectively. For the latter cases, a drastic reduction in PL lifetime is observed upon CNT wrapping.

(MIR) spectral region also for excitation energies smaller than the polymer band gap. Comparing a sample of purified polymer-wrapped CNTs with one containing excess polymer, we are furthermore able to prove that the polarons predominantly reside on those polymer chains directly attached to the nanotubes. Quantum chemical calculations show a significant mixing of the first excited state, especially for the thiophene. This hybrid state can dissociate into free charge carriers, of which the electron is located on the CNTs and the hole on the polymer chain and thereby explains the polaron absorption band for below-gap excitation.

We believe that a detailed understanding of the polymer's role on the photophysics of wrapped CNT composites is essential to further the community's understanding of this important material class. Our experimental results, supported by the modeling, thus enlighten the hybrid nature of the electronic states in polymer-wrapped CNTs. We furthermore propose that the FTIR technique is an essential tool for attaining deeper insight into the relevance of these mixed electronic states, ultimately allowing for designing better-performing polymer–CNT composites.

The spectroscopic properties of polymer-wrapped CNTs change greatly with the sample quality (e.g., amount of residual metallic tubes or bundles) and preparation technique (film vs solution, casting method). We thus start by describing the general behavior of our films before focusing on the interaction mechanism of the different polymers with the CNTs, for which the energy levels are depicted in Figure 1a. The absorption spectra in Figure 1b include neat P3DDT as well as the CNT sample (in solution and as a drop-cast film). P3DDT exhibits a comparatively narrow band gap and was previously shown to exhibit a high dispersion yield for HiPCO CNTs with a diameter of approximately 1 nm.¹³ The polymer absorbs most strongly from 1.9 to 3.5 eV, a spectral region with few nanotube transitions. The spectrum of P3DDT, when wrapping CNTs, exhibits distinct peaks at 2.3 and 2.05 eV, which indicate a strong π – π interaction between wrapping polymer chains and the CNTs.¹⁴ Interestingly, whether the tubes are in solution or in a film has a negligible impact on the position of their ground-state transition (S_{11}) (also see Figure S1). From the ratio of the polymer absorption to the S_{11} transitions of the tubes, we infer that the amount of unbound polymer in this purified sample is negligible, as was previously demonstrated by our group.⁵ The

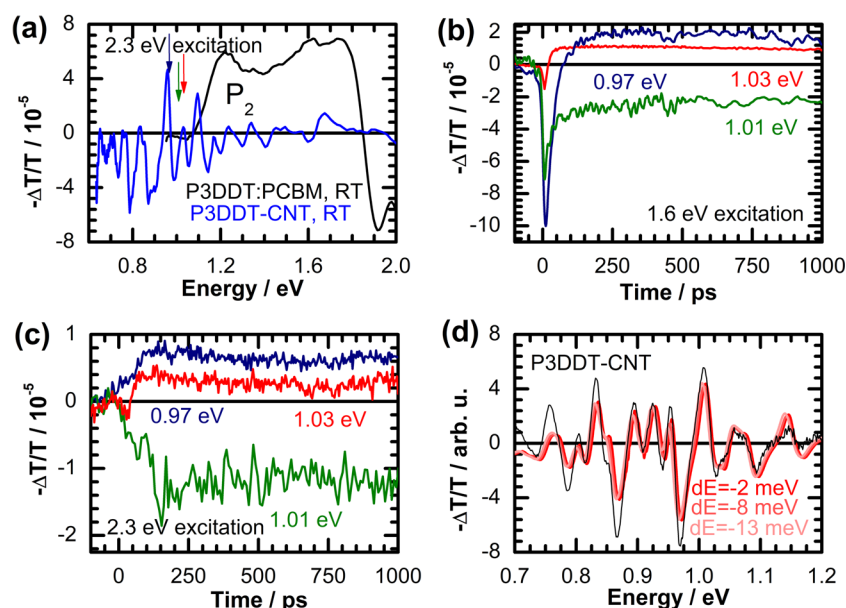


Figure 3. NIR quasi steady-state PIA ($f = 141 \text{ Hz}$) of P3DDT:PCBM and P3DDT-CNTs (a). The latter exhibits narrow signals attributable to the CNTs, but the characteristic P_2 absorption of the polymer cannot be observed. Transient spectra at three selected energies upon CNT (b) and polymer excitation (c) include long-lasting signals. Steady-state photoinduced absorption spectrum of P3DDT-wrapped tubes along with calculated spectra (d). The latter were generated for a red-shifted absorption as outlined in the main text.

same is true for the second investigated sample containing CNTs wrapped with PF12 (Figure S2a).

In contrast to highly monochiral samples, intertube charge- or energy-transfer processes from small to large diameter tubes could dominate in our films.^{11,12} The steady-state PL intensity in Figure 2a, however, generally follows the absorption profile of the respective sample in solution (also consider Figure S3). This shows that on-site radiative recombination on the tubes competes favorably with intertube exciton migration. We note that when omitting the ultrasonic treatment prior to casting the sample, the PL intensity shifts toward lower energies (Figure S4), which we attribute to an efficient energy transfer in bundles and aligned tubes. The PL intensity, in either case, is distinctly low, which is in agreement with the determined PL lifetimes of approximately 30 ps (Figure 2b) and previous reports.^{10,15} The steady-state emission profile of the polymers in Figure 2a slightly changes upon wrapping because of the altered chain conformation, analogously to the absorption spectra discussed above. The PL lifetime of both polymers is reduced by a factor of 10 for both decay components (Figure 2c,d), which could be explained by both an energy- or a charge-transfer toward the wrapped tubes.

For a deeper understanding of the transfer processes, we turn to pump–probe techniques, as they allow for investigating possible charge carrier signatures. In semiconducting polymers, charge carriers lead to the formation of additional absorption bands, of which one is commonly found at energies slightly smaller than the band gap (often referred to as P_2 transition). A second one emerges in the MIR spectral region (generally called P_1). In the quasi-steady state, upon excitation with 2.3 eV (532 nm), the P_2 absorption forms around 1.23 eV for P3DDT blended with the electron acceptor PCBM (Figure 3a). When wrapped around CNTs, however, there is no such distinct feature observable. In contrast, this sample exhibits an additional rich pattern of narrow absorption and bleach transitions. The presence of these pronounced features points to long-lived species formed on the single nanotubes.

Examining the transient behavior at three selected probe energies (Figure 3b), we observe a strongly negative response for all chiralities at short delay times, when pumping in the region of CNT absorption (1.6 eV, 780 nm). A constant signal, corresponding to the steady-state sign, is reached after approximately 150 ps. We attribute the long-lasting component to charges that form upon nanotube excitation^{16,17} and note that the ultrafast response is complex and may involve phenomena such as the formation of singlets, triplets, biexcitons, and trions.^{18–20} For an excitation energy of 2.3 eV (532 nm), i.e., in the absorption region of the polymer, we observe the same trends at long delay time, but without the dip at early times (Figure 3c). This is suggestive of a charge transfer from the polymer, rather than an energy transfer, for which we would expect similar dips at early times.

The formation of charges in monochiral CNTs has been greatly investigated, and there is a consensus that besides the prominent ground-state bleach, several absorption bands form upon photoexcitation.^{4,12,21–23} The most prominent of the latter is the trion peak, which involves the generation of a three-particle state (2 holes and 1 electron or vice versa) and exhibits an energy lower than the S_{11} transition. We sought to explain the PIA signals of the CNTs by considering the ground-state bleach (GSB), i.e., the depopulation of the electronic ground state of the CNTs, and a trion absorption as discussed in the Supporting Information, but we are unable to find a good agreement with our experimental data (Table S1 and discussion). In contrast, we can mimic the resulting spectrum by assuming a small red-shift of the ground-state absorption of the CNTs under illumination (Figure 3d), similar to that previously proposed^{17,23} and explained in the Supporting Information. This red-shift was previously assigned to a Stark effect.^{17,23} Although we consider this to be a likely mechanism, we note that a change in charge carrier concentration itself might be responsible for such a red-shift, as excess charges were reported to lead to a drastic reduction in the CNT fundamental band gap.^{24,25}

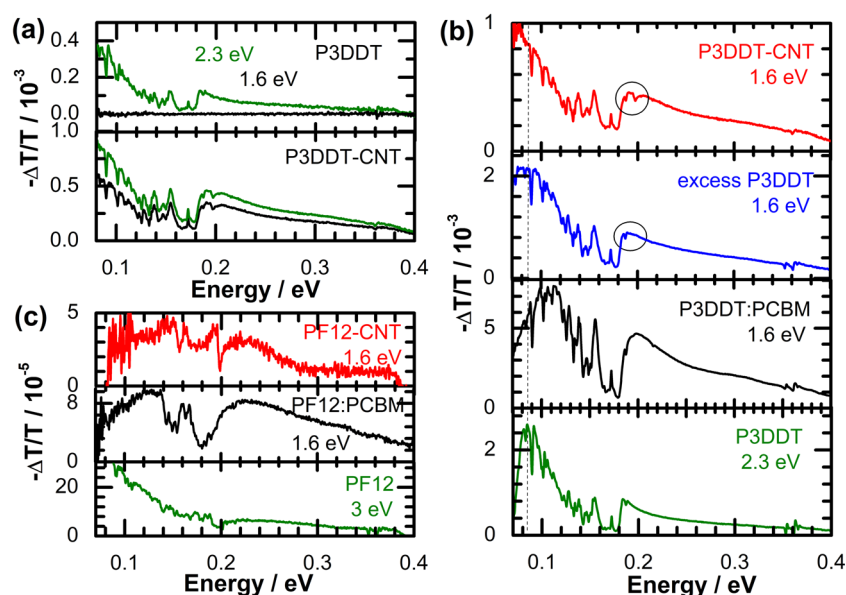


Figure 4. MIR PIA of P3DDT-containing samples upon above and below polymer gap excitation (a) and comparison of the band's position in different samples (b) (the numbers denote the pump energy). PF12-related PIA for different samples (c).

Considering the above measurements in the NIR spectral region, we can infer that charges are generally formed on the CNTs, and for the polymer excitation, there is evidence of an electron transfer toward the nanotubes. Because this process should also lead to a so far elusive hole remaining on the polymer, we turn to the MIR spectral region for further investigation.

Figure 4a depicts the MIR photoinduced absorption of neat P3DDT (top) and when wrapped around CNTs (bottom), upon excitation above and below the polymer band gap. In both samples, there is a broad absorption band peaking around 0.1 eV, when exciting above the polymer band gap energy, which we attribute to the formation of polarons on the polymer (as validated by the P3DDT:PCBM spectra reported in Figures S6 and S7).^{26–28} The narrow features superimposed are infrared active vibrations (IRAVs) due to the interplay of molecular vibrations with charges.^{27,29} Note that the signals' position is independent of the excitation energy and varies only in strength (see Figure S5 for normalized spectra). We furthermore add that the precise shape and origin of the PIA band is complex, and we are here content to use it as a fingerprint for the polaron formation on the polymer.^{26–28} The black lines in Figure 4a indicate the spectra obtained for excitation at 1.6 eV, i.e., below the polymer band gap energy. As expected, it remains flat for the neat polymer, while for the CNT sample, the same polaron signature can be observed as for above gap excitation. Photon absorption of the CNTs thus leads to the formation of charges on the polymer, as uniquely evidenced by the spectral signature of their polarons.

As the position of the absorption band in the MIR works as a highly sensitive probe for the environment of the charge, this effect is examined by comparing the position of the maximum of the P_1 signal, as displayed in Figure 4b. The position shifts to lower energies from the blend with the electron acceptor PCBM over the neat case to the wrapped tubes. This trend underlines the strong π – π interaction between the wrapping polymer, carrying the charge, and the CNTs noted above for the absorption and PL spectra (Figures 1b and 2a).³⁰ Although the employed samples were highly purified, the presence of

unattached polymer chains cannot per se be excluded, and free excess polymer could take up charge carriers from the wrapping chains to stabilize them. To clarify the location of the observed carriers, we added a sample, for which the purified CNTs were mixed with excess P3DDT prior to deposition, to ensure the presence of unbound chains between the tubes (also consider Figures S9 and S10). Indeed, the PIA spectrum in Figure 4b displays a shift of the envelope toward higher energy. For the purified samples, we therefore conclude that charge carriers reside on the chains wrapped around the CNTs.

Supporting this claim, distinct differences in the vibrational signals emerge between the CNT samples in the presence and absence of excess polymer. In the purified case, a narrow feature at 0.197 eV (1594 cm^{-1}) can be observed, which is not present in the sample where extra polymer has been added. This spectral feature coincides with the CNT G-band optical phonons.³¹ Given its asymmetric shape, we attribute this feature to a Fano resonance³² between the energetically broad electronic background of the polaron and the narrow vibration. This feature is thus observable only if the CNTs are in proximity of the charge. Conversely, the CH-modes of the polymer around 0.36 eV (approximately 2990 cm^{-1}) almost vanish for the purified CNTs because of the small amount of polymer.

The formation of a polymer polaron signature upon below band gap excitation is a surprising observation. Another explanation one might invoke would be generated through CNT excitation into higher manifolds (S_{22}), which could transfer toward the polymer prior to thermalization. Thermalization into the S_{11} manifold, however, was reported to occur on an ultrafast time scale shorter than 100 fs,³³ which is why we consider this mechanism unlikely. Nonetheless, we investigated a sample of P3DDT-CNT upon directly S_{11} exciting at 1.16 eV (1064 nm), as shown in Figure S12, and find a broad absorption and the same IRAVs as for higher-energy excitation. We can thus conclusively dismiss ultrafast charge transfer from higher manifolds as the origin of the polaron formation. To verify that this observation is not an exception for a particular

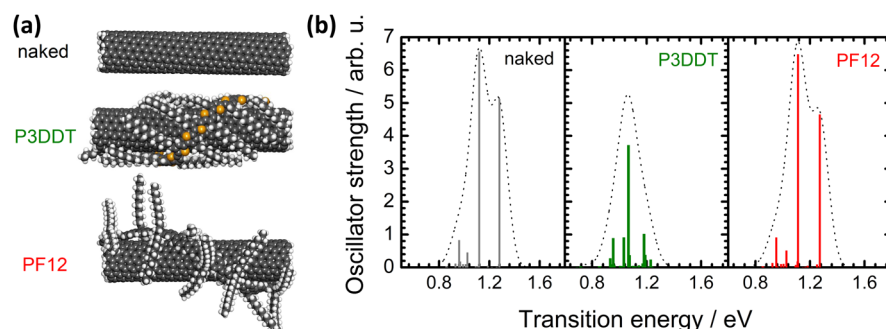


Figure 5. Geometric optimization of oligomers wrapping a CNT (a). Calculated contributions to the first excitation of naked CNTs and when wrapped by either P3DDT or PF12 (b). For P3DDT:CNT, the states are strongly affected by hybridization.

material, we also carried out the same investigation with CNTs wrapped with the wider band gap polymer PF12.

Similar to the case of P3DDT, we first investigate the PIA response of the neat polymer and of a blend with PCBM to determine the polaron signature. As can be seen from Figure S13, exciting the neat polymer above the band gap (at 3 eV; 410 nm) gives rise to a narrow and strong photoinduced absorption peak at 1.45 eV. This signal has previously been attributed to a triplet absorption.³⁴ In the MIR, we can also observe a weak band below 0.4 eV and the formation of IRAVs. As expected, exciting the polymer below the band gap (2.3 eV) does not create any absorption feature. In contrast, the blend with PCBM exhibits the same spectral features for both cases and even for 1.6 eV excitation (Figures S14 and S15), notably also the IRAVs. The charge formation for below polymer gap excitation here is due to a hole transfer from PCBM toward the polymer.

Turning to the CNT sample, we again find that every pump energy (3, 2.3, and 1.6 eV; Figure S16) generates a distinct polaron band in the MIR, which is similar to the one observed for the blend with PCBM (Figure 4c). We conclude that even for below polymer gap excitation, polarons are formed on the chains. Similarly to the P3DDT case, we also find the narrow feature at 0.197 eV linked to CNT phonons, indicating that chains wrapped around the tubes carry the holes.

Our findings thus show that the common way of depicting the energy levels as in Figure 1a is not reflecting the actual energy alignment for polymer-wrapped CNTs. We are of the opinion that the close proximity of the two entities and the interaction of their respective π -systems (as seen by the changes in the PL and absorption spectra) create a new hybrid system with states shared between the components, similarly to what was observed in the “pea in a pod” systems of small molecules filled into CNTs.³⁵ This hybridization of states might help to explain why we do not observe an energy barrier in our transport measurements using field effect transistors.^{3,5,36} Furthermore, we observe distinctly different threshold voltages, i.e., the gate voltage for switching from n-type to p-type transport in the channel, when using different wrapping polymers.⁵ A density of states that is strongly affected by the wrapping polymer would help to explain these differences.

To prove the hybrid nature of the excited system, we examined the low-lying excited states of P3DDT:CNT and PF12:CNT by means of the quantum chemical method ZINDO/S-CI. In this method, the wave function of the molecular excited state is written as a linear combination of Slater determinants representing all of the singly excited states that can be built from the reference ground-state determinant.

The hybrid systems were modeled as a molecule comprising a finite (8,6) nanotube and an oligomer wrapping the nanotube in a helical conformation (Figure 5a). The ground-state conformations were optimized within a density functional derived semiempirical method, as described in Methods in the Supporting Information.

Figure 5b depicts the calculated absorption spectra alongside the absorption of a naked (8,6) nanotube for comparison. First, we note that, because of the finite size of the system, the main S_{11} transition peak of the naked nanotube is split into two main contributions. Additionally, in the P3DDT:CNT system, the peaks are split farther because of a strong polymer–nanotube interaction, which also shifts the transitions to lower energy. Table S2 displays the most important contributions that form these excited states and the corresponding coefficients associated with the probability of a particular excitation. The leading excitations are $H - 8 \rightarrow L$ and $H - 1 \rightarrow L + 1$ [$H - i$ denotes i th level below the highest occupied molecular orbital (HOMO) and $L + i$ the i th level above the lowest unoccupied molecular orbital (LUMO)], and most molecular orbitals involved are mainly localized on the nanotube. In agreement with our proposition, however, there is a considerable contribution of orbitals presenting a large degree of hybridization between the polymer and the CNT. Some examples are depicted in Figure S17. Apart from the transition $H - 7 \rightarrow L + 10$ (HOMO–LUMO polymer transition) appearing in the 1.07 eV excited state, all other transitions involving hybridized orbitals exhibit their starting orbital with a large contribution from the polymer, and the final orbital is localized on the nanotube. These excitations may thus, in effect, lead to an electron transfer from the polymer to the nanotube at an excitation energy normally assumed to be purely due to the CNTs.

The right panel of Figure 5 shows the spectrum of the PF12:CNT system, which is similar to the spectrum of the naked nanotube shown on the left. There is some degree of hybridization of the molecular states, but to a significantly smaller proportion than for the P3DDT:CNT system. For comparison, we show the CNT absorption region for both samples in Figure S2b and observe the expected red-shifted peaks for the P3DDT sample. We note, however, that besides selecting different chiralities, the changed permittivity of the tube environment due to the different polymers will also affect the peak position. This is also in good agreement with the experimentally determined smaller polaron signal as shown in Figure 4c. The reason for this weaker interaction lies in the geometry of the polymer-wrapped nanotube. As the fluorene units of PF12 are longer and stiffer than the thiophene ring of

P3DDT, besides the geometrical constraints imposed by the dodecyl chains attached at the 9 position, the fluorene rings do not adsorb to the nanotube surface as close as the thiophenes.

In conclusion, we investigated the interaction of excited states in films of polymer-wrapped single-walled carbon nanotubes, with a polythiophene and a polyfluorene as wrapping agent. We show that photon absorption leads to the formation of a polaron on the respective polymer, independent of whether the excitation energy lies above or below the polymer band gap. This process cannot be explained by considering the classical energy level scheme for two separated materials, but as we show through quantum chemical calculations, there is strong proof for the hybridized nature of the excited states of this material class. Our insights underline the strong interaction of polymers with CNTs and will help to better understand and explain observations in optoelectronic applications based on these hybrid materials.

We propose that further investigations should aim at a more refined understanding of the charge formation mechanism for below polymer band gap excitation, in particular on an ultrafast time scale. This will help to elucidate whether the generation of free charge carriers on the polymer is a prompt process or requires the dissociation of intermediate species.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpclett.7b02553](https://doi.org/10.1021/acs.jpclett.7b02553).

Additional absorption spectra focusing on the NIR spectral region for PF12-wrapped CNTs, PL spectra of polymer-wrapped CNTs when omitting proper ultrasonication, overview and normalized PIA spectra for several relevant samples, discussion of the origin of steady-state PIA signals of CNTs, calculation of trion energies as well as the tables for orbital composition and illustration of excited states for P3DDT-wrapped CNTs (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

S.K. acknowledges the Ubbo Emmius foundation of the University of Groningen and the research training group GRK 1896 of the German Research foundation for funding of his Ph.D.

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